

# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>CS/K-21873/A</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/EP 99/08530</b>	International filing date (day/month/year) <b>06/11/1999</b>	(Earliest) Priority Date (day/month/year) <b>17/11/1998</b>
Applicant <b>CIBA SPECIALTY CHEMICALS HOLDING INC.et.al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.



It is also accompanied by a copy of each prior art document cited in this report.

### 1. Basis of the report

a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.



the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing :



contained in the international application in written form.



filed together with the international application in computer readable form.



furnished subsequently to this Authority in written form.



furnished subsequently to this Authority in computer readable form.



the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.



the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ Certain claims were found unsearchable (See Box I).

3. ☐ Unity of invention is lacking (see Box II).

4. With regard to the title,



the text is approved as submitted by the applicant.



the text has been established by this Authority to read as follows:

5. With regard to the abstract,



the text is approved as submitted by the applicant.



the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No.



as suggested by the applicant.



because the applicant failed to suggest a figure.



because this figure better characterizes the invention.



None of the figures.

## INTERNATIONAL SEARCH REPORT

International Application No

EP 99/08530

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09D201/00 C08K5/3492 C07D405/14

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D C08K C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 24408 A (HOBEL KLAUS ;BERG KEIMPE JAN VAN DEN (NL); AKZO NOBEL NV (NL); NOO) 10 July 1997 (1997-07-10) cited in the application page 15, paragraph 2 -page 16, paragraph 1; examples ---	1-3,6-8, 11
A	DE 41 29 752 A (DAINIPPON INK & CHEMICALS) 11 March 1993 (1993-03-11) example 15 ---	1,3,8
A	EP 0 529 361 A (DAINIPPON INK & CHEMICALS) 3 March 1993 (1993-03-03) page 4, line 45 - line 47; example 1 -----	1,3

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"S" document member of the same patent family

Date of the actual completion of the international search

9 March 2000

Date of mailing of the international search report

24/03/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Engel, S

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 99/08530

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 9724408	A	10-07-1997	NL	1002008 C	03-07-1997
			AT	189472 T	15-02-2000
			DE	69606560 D	09-03-2000
			EP	0871682 A	21-10-1998
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DE 4129752	A	11-03-1993	JP	5202023 A	10-08-1993
-----					
EP 0529361	A	03-03-1993	JP	5039336 A	19-02-1993
			DE	69205767 D	07-12-1995
			DE	69205767 T	25-04-1996
			US	5304628 A	19-04-1994
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From the INTERNATIONAL BUREAU

PCT

NOTICE INFORMING THE APPLICANT OF THE  
COMMUNICATION OF THE INTERNATIONAL  
APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

Date of mailing (day/month/year) 25 May 2000 (25.05.00)		<b>IMPORTANT NOTICE</b>	
Applicant's or agent's file reference CS/K -21873/A			
International application No. PCT/EP99/08530	International filing date (day/month/year) 06 November 1999 (06.11.99)	Priority date (day/month/year) 17 November 1998 (17.11.98)	
Applicant CIBA SPECIALTY CHEMICALS HOLDING INC. et al			

To:

CIBA SPECIALTY CHEMICALS HOLDING  
INC.  
Patentabteilung Ressort P/TM/GI LE 5  
Klybeckstrasse 141  
CH-4057 Basel  
SUISSE

5. Juni 2000		
PATA	PATB	SES

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:  
CN,JP,KR,US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:  
BR,EP

The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on 25 May 2000 (25.05.00) under No. WO 00/29497

**REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)**

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a demand for international preliminary examination must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

**REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))**

If the applicant wishes to proceed with the international application in the national phase, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer J. Zahra
Facsimile No. (41-22) 740.14.35	Telephone No. (41-22) 338.83.38

**PCT**

**NOTIFICATION OF THE RECORDING  
 OF A CHANGE**

(PCT Rule 92bis.1 and  
 Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

VANTICO AG  
 Patents/Scientific Information  
 Klybeckstrasse 200  
 CH-4057 Basel  
 SUISSE

<b>Date of mailing (day/month/year)</b> 01 August 2000 (01.08.00)	<b>IMPORTANT NOTIFICATION</b>
<b>Applicant's or agent's file reference</b> CS/K -21873/A	
<b>International application No.</b> PCT/EP99/08530	<b>International filing date (day/month/year)</b> 06 November 1999 (06.11.99)

1. The following indications appeared on record concerning:

☒ the applicant ☐ the inventor ☐ the agent ☐ the common representative

<b>Name and Address</b> CIBA SPECIALTY CHEMICALS HOLDING INC. Klybeckstrasse 141 CH-4057 Basel Switzerland	<b>State of Nationality</b> CH	<b>State of Residence</b> CH
	<b>Telephone No.</b>	
	<b>Facsimile No.</b>	
	<b>Teleprinter No.</b>	

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☒ the person ☒ the name ☒ the address ☐ the nationality ☐ the residence

<b>Name and Address</b> VANTICO AG Klybeckstrasse 200 CH-4057 Basel Switzerland	<b>State of Nationality</b> CH	<b>State of Residence</b> CH
	<b>Telephone No.</b>	
	<b>Facsimile No.</b>	
	<b>Teleprinter No.</b>	

3. Further observations, if necessary:

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☐ the International Searching Authority ☒ the elected Offices concerned  
☒ the International Preliminary Examining Authority ☐ other:

<b>The International Bureau of WIPO</b> 34, chemin des Colombettes 1211 Geneva 20, Switzerland	<b>Authorized officer</b>  C. Cupello
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

## PATENT COOPERATION TREATY

PCT

NOTIFICATION OF THE RECORDING  
OF A CHANGE(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

VANTICO AG  
Patents/Scientific Information  
Klybeckstrasse 200  
CH-4057 Basel  
SUISSE

Date of mailing (day/month/year)

01 August 2000 (01.08.00)

Applicant's or agent's file reference

CS/K -21873/A

## IMPORTANT NOTIFICATION

International application No.

PCT/EP99/08530

International filing date (day/month/year)

06 November 1999 (06.11.99)

1. The following indications appeared on record concerning:

☐ the applicant ☐ the inventor ☐ the agent ☒ the common representative

Name and Address

CIBA SPECIALTY CHEMICALS HOLDING  
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Teleprinter No.

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☒ the person ☒ the name ☒ the address ☐ the nationality ☐ the residence

Name and Address

VANTICO AG  
Patents/Scientific Information  
Klybeckstrasse 200  
CH-4057 Basel  
Switzerland

State of Nationality

State of Residence

Telephone No.

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3. Further observations, if necessary:

4. A copy of this notification has been sent to:

☒ the receiving Office ☐ the designated Offices concerned  
☐ the International Searching Authority ☒ the elected Offices concerned  
☒ the International Preliminary Examining Authority ☐ other:The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

C. Cupello

Telephone No.: (41-22) 338.83.38

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
United States Patent and Trademark  
Office  
Box PCT  
Washington, D.C. 20231  
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing:

25 May 2000 (25.05.00)

International application No.:

PCT/EP99/08530

Applicant's or agent's file reference:

CS/K -21873/A

International filing date:

06 November 1999 (06.11.99)

Priority date:

17 November 1998 (17.11.98)

Applicant:

RICKERT, Christoph et al

1. The designated Office is hereby notified of its election made:



in the demand filed with the International preliminary Examining Authority on:

06 April 2000 (06.04.00)



in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was



was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer:

J. Zahra

Telephone No.: (41-22) 338.83.38



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> <b>C09D 201/00, C08K 5/3492, C07D 405/14</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/29497</b> <b>(43) International Publication Date:</b> 25 May 2000 (25.05.00)
<b>(21) International Application Number:</b> PCT/EP99/08530 <b>(22) International Filing Date:</b> 6 November 1999 (06.11.99) <b>(30) Priority Data:</b> 2299/98 17 November 1998 (17.11.98) CH <b>(71) Applicant (for all designated States except US):</b> CIBA SPECIALTY CHEMICALS HOLDING INC. [CH/CH]; Klybeckstrasse 141, CH-4057 Basel (CH). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> RICKERT, Christoph [CH/CH]; Hauptstrasse 130, CH-4153 Reinach (CH). FRANÇOIS, Jacques [FR/FR]; 36, rue de Lecture, F-68300 Saint Louis (FR). PICOT, Jean-Bernard [FR/FR]; 20, rue du Dr. Schweitzer, F-92160 Antony (FR). <b>(74) Common Representative:</b> CIBA SPECIALTY CHEMICALS HOLDING INC.; Patentabteilung, Klybeckstrasse 141, CH-4057 Basel (CH).		<b>(81) Designated States:</b> BR, CN, JP, KR, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> CROSSLINKING AGENT FOR CARBOXYL-CONTAINING POLYMERS IN HEAT-CURABLE SYSTEMS  <b>(57) Abstract</b>  Crosslinking agent for heat-curable carboxyl-containing polymers, in particular for systems containing carboxyl-terminated polyesters, carboxyl-containing acrylate and/or methacrylate polymers, which crosslinking agent consists of at least one cyclocarbonate group-containing isocyanurate compound into which at least one catalyst has been incorporated in dissolved or dispersed form prior to the crosslinking reaction, and heat-curable systems containing such a crosslinking agent, in particular paint systems and powder coating compositions.		



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Crosslinking agent for carboxyl-containing polymers in heat-curable systems

The present invention relates to crosslinking agents (hardeners) for heat-curable systems containing carboxyl-containing polymers, in particular to systems containing carboxyl-terminated polyester polymers, carboxyl-containing acrylate polymers and/or carboxyl-containing methacrylate polymers. This invention relates in particular to a crosslinking agent based on cyclocarbonate group-containing isocyanurate compounds.

It is known to use cyclocarbonate groups containing isocyanurates to replace the analogous polyglycidyl compounds as crosslinking agents in curable compositions containing carboxyl-containing polymers, such as carboxyl-terminated polyesters, carboxyl-containing acrylates and/or methacrylate polymers. WO 97/24408, for example, discloses curable systems containing at least one carboxyl-terminated polyester compound as binder, one cyclocarbonate group-containing isocyanurate compound and one polyglycidyl compound as crosslinking agent, an accelerator (catalyst) as well as other per se known additives. The use of a cyclocarbonate group-containing isocyanurate compound is regarded as an alternative for using corresponding polyglycidyl compounds. As a consequence of the curing process, carbon dioxide (CO<sub>2</sub>) is liberated from the cyclocarbonate group and escapes, which may result in foam formation at coating thicknesses of more than 20 µm, unless the composition contains a certain amount of at least one glycidyl compound. The presence of the glycidyl compound results in a reduction of the foam formation so that coating thicknesses of up to 100 µm can be produced without any substantial interfering foam formation. However, there still remain the different reaction rates of the two crosslinking agents towards the binder so that it is necessary to carry out curing at relatively high temperatures. In consequence, the curing of the glycidyl groups proceeds relatively quickly, which impedes the carbon dioxide's escape without bubble formation. If the cyclocarbonate group-containing compounds have a melting point above 120°C or 130°C and if these compounds are furthermore sparingly soluble or insoluble in the binder, then the mentioned disadvantages are augmented by the different reaction rates of the two crosslinking agents with the binder.

Surprisingly, it has now been found that the cited disadvantages are substantially or completely overcome if the catalyst to be used for crosslinking the cyclocarbonate groups is incorporated in the cyclocarbonate group-containing isocyanurate compound beforehand by

a suitable method and if the crosslinking agent thus modified is only then added to the curable system. In this manner it is possible to start curing the system at a comparatively low temperature, often below the melting point of the cyclocarbonate group-containing compounds. Moreover, less catalyst is required, which reduces the costs. The carbon dioxide can escape at a lower temperature, i.e. when curing is less advanced, substantially reducing the foaming tendency. The escape of the carbon dioxide can start at a lower temperature and stretch over a longer period of time, which in turn makes it possible to produce thicker coatings, i.e. coating thicknesses of more than 100  $\mu\text{m}$  and, where necessary, of up to 200  $\mu\text{m}$ , without foam formation.

The present invention is defined in the patent claims. This invention relates in particular to a crosslinking agent (hardener) for heat-curable carboxyl-containing polymers, especially for systems containing carboxyl-terminated polyesters, carboxyl-containing acrylate and/or methacrylate polymers, which crosslinking agent consists at least of one cyclocarbonate group-containing isocyanurate compound, which is characterised in that said cyclocarbonate group-containing isocyanurate compound contains at least one catalyst in dissolved or dispersed form, i.e. this catalyst is incorporated separately into the isocyanurate compound prior to the crosslinking reaction.

The novel crosslinking agent is preferably prepared by dissolving a cyclocarbonate group-containing isocyanurate compound in a suitable solvent, dissolving or dispersing therein at least one catalyst and then removing the solvent again.

Accordingly, this invention relates to a process for the preparation of the novel crosslinking agent, which comprises dissolving a cyclocarbonate group-containing isocyanurate compound in a suitable solvent, dissolving or dispersing therein at least one catalyst and then removing the solvent again. This invention also relates to the crosslinking agents which are prepared or obtainable in this manner.

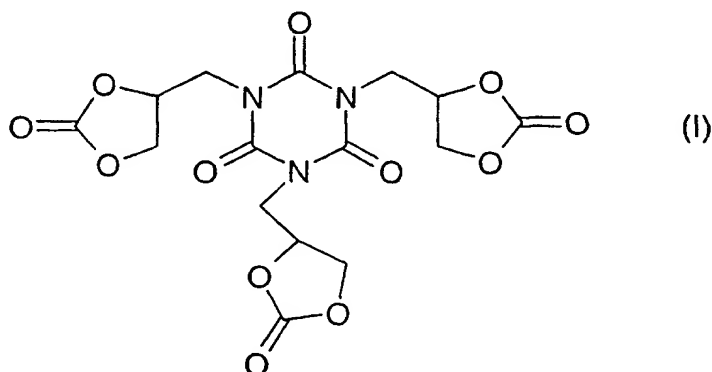
This invention also relates to the use of the novel crosslinking agent as hardener in heat-curable carboxyl-containing polymers, in particular in systems containing carboxyl-terminated polyesters, carboxyl-containing acrylate and/or methacrylate polymers, preferably in heat-curable paint systems and, especially, in heat-curable powder coating compositions.

Such heat-curable systems, paint systems or powder coating compositions preferably comprise (i) as binder at least one carboxyl-containing polymer, more preferably a carboxyl-terminated polyester and/or a carboxyl-containing acrylate and/or methacrylate polymer, (ii) a novel crosslinking agent, (iii) optionally one or several glycidyl compound(s) and at least one catalyst for the crosslinking reaction of said glycidyl compound(s) together with the carboxyl-containing polymer, and (iv) per se customary other additives.

The cyclocarbonate groups contained in the crosslinking agent can be prepared by reacting the corresponding glycidyl group-containing isocyanurate compound with carbon dioxide in the presence of a catalyst, preferably a basic compound, part or all of the glycidyl groups present in the molecule converting into the cyclocarbonate group. During the crosslinking reaction with the carboxyl group, i.e. during the curing process, the cyclocarbonate group releases the carbon dioxide absorbed during the synthesis. The preparation of the cyclocarbonate group from the glycidyl group is known per se and is described, inter alia, in WO 97/24408, pages 6 and 7 with additional source references, as cited at the outset.

The cyclocarbonate group-containing isocyanurate compounds which may be used according to this invention preferably have a melting point of at least 120°C, more preferably of at least 130°C and, particularly preferably, of at least 140°C, and are normally sparingly soluble or insoluble in the binder, i.e. their solubility is below 20 gram, and often below 10 gram, of isocyanurate compound per 100 gram of binder.

The cyclocarbonate group-containing isocyanurate compound is preferably a tris(2-oxo-1,3-dioxolanyl-4-methyl)isocyanurate according to the following formula (I):



The compound of formula (I) is listed in the form which is usually preferred. In analogy to the compound of formula (I) it is also possible to use a compound which contains only one single or two cyclocarbonate group(s), the remaining groups being in the form of glycidyl radicals. The compound of formula (I) preferably contains not more than 35 mol-% of epoxy groups, particularly preferably not more than 5 mol-%.

The novel crosslinking agent which contains at least one catalyst is preferably prepared by dissolving a cyclocarbonate group-containing isocyanurate compound in a suitable solvent, dissolving or dispersing therein at least one catalyst and then removing the solvent again. The solvents used may be suitable inorganic and organic solvents, for example lactones, dimethylsulfoxide, amidic solvents, such as N-methylpyrrolidone or dimethylformamide. A preferred solvent is  $\gamma$ -butyrolactone.

To achieve a sufficient crosslinking reaction, the novel crosslinking agent contains the catalyst in an amount from 0.01 % by weight to 20 % by weight, preferably from 0.1 % by weight to 10 % by weight and, more preferably, from 5 % by weight to 10 % by weight, based on the weight of the cyclocarbonate group-containing isocyanurate compound.

The novel crosslinking agent, for example the tris(2-oxo-1,3-dioxolanyl-4-methyl)isocyanurate compound, into which e.g. an ethyltriphenylphosphonium bromide has been incorporated in a concentration of 0.01 to 20 % by weight (based on the weight of the cyclocarbonate group-containing isocyanurate compound), is used in concentrations from 1 to 20 % by weight, preferably in concentrations from 2 to 10 % by weight, based on the sum of the weight of crosslinking agent and binder.

Besides the novel crosslinking agent, the curable system preferably also contains at least one crosslinking glycidyl compound. The weight ratio of the amount of the novel crosslinking agent on the one hand (calculated on the weight of the cyclocarbonate group-containing isocyanurate compound(s) present therein) to the amount of the crosslinking glycidyl compound(s) on the other hand, is preferably from 0.1 to 2.0, more preferably from 0.1 to 1.0. A ratio from 0.2 to 0.5 is particularly preferred. The crosslinking glycidyl compound is in this case added to the curable composition separately, and the corresponding catalyst is also added to the composition separately. The kind and amount of the separately added catalyst is adjusted to, or calculated for, the kind and amount of the separately added

glycidyl compound. The catalysts used for the glycidyl compounds are preferably added in per se known concentrations used for conventional heat-curable systems based on carboxyl-terminated polyesters and glycidyl compounds.

According to this invention it is thus preferred to use on the one hand a catalyst which acts selectively predominantly or exclusively on the cyclocarbonate group-containing isocyanurate compound, the respective catalyst being separately incorporated to this purpose into the isocyanurate compound prior to the crosslinking reaction. On the other hand, a catalyst is also added to the curable composition which acts predominantly and preferably selectively on the glycidyl compound.

Examples of suitable accelerators (catalysts) which accelerate the crosslinking reaction of the cyclocarbonate group-containing isocyanurate compounds with the carboxyl-containing polymers and the liberation of carbon dioxide during the corresponding crosslinking, are in particular compounds acting as Lewis acids and Lewis bases and also certain inorganic salts and their hydrates. Corresponding examples are  $\text{FeSO}_4$ ,  $\text{NaHSO}_4$ ,  $\text{CeSO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{ZnCl}_2$ ,  $\text{Na}_2\text{CO}_3$ , phosphonic acid, p-toluenesulfonic acid and dimethylsulfonic acid. Ammonium salts and/or phosphonium salts are preferred. Examples are quaternary ammonium salts such as tetraalkyl ammonium halides, aryl- and alkyl-substituted ammonium halides, such as tetramethyl ammonium bromide, trimethylbenzyl ammonium hydroxide, 2-hydroxypyridine, trimethylbenzyl ammonium methoxide, phenyltrimethyl ammonium chloride, phenyltrimethyl ammonium bromide, phenyltrimethyl ammonium hydroxide, phenyltrimethyl ammonium iodide, phenyltrimethyl ammonium tribromide, the sodium salt of phosphocholine chloride, stearyl ammonium bromide, tetra-n-amyl ammonium iodide, tetra-n-butyl ammonium bromide, tetra-n-butyl ammonium hydroxide, tetra-n-butyl ammonium phosphate, tetra-n-decyl ammonium trichloride, tetraethyl ammonium hydroxide, tetraethyl ammonium tetrafluoroborate, tetramethylguanidine, acetylcholine bromide, alkyldimethylbenzyl ammonium chloride, benzylcholine bromide, benzyl-n-butyl ammonium bromide, bis(tetra-n-butyl ammonium)dichromate, trimethyl vinyl ammonium bromide; phosphonium salts, for example ethyltriphenylphosphonium bromide, DBU (1,8-diazabicyclo(5.4.0)undec-7-ene(1,5-5)), tetramethyl ammonium chloride (TMAC), allyltriphenylphosphonium chloride, benzyltriphenylphosphonium chloride, bromomethyltriphenylphosphonium bromide, 2-dimethylaminoethyltriphenylphosphonium bromide, ethoxycarbonylphosphonium bromide, n-heptyltriphenylphosphonium bromide, methyltriphenylphosphonium bromide,

tetrakis(hydroxymethyl)phosphonium sulfate and tetraphenylphosphonium bromide.

Phosphonium salts are preferred, in particular the cited phosphonium halides.

Ethyltriphenylphosphonium bromide is particularly preferred.

As mentioned above, the curable system preferably contains besides the novel crosslinking agent also at least one crosslinking glycidyl compound. Preferred crosslinking glycidyl compounds are those which contain at least two 1,2-epoxy groups in the molecule and which may also be called polyglycidyl compound(s). It is preferred to use a mixture of polyglycidyl compounds, for example a mixture of diglycidyl and triglycidyl compounds. Such compounds are known per se and are described in the literature. A suitable selection can usually be made from the known glycidyl compounds.

In this invention it is preferred to use glycidyl compounds such as those described, inter alia, in EP-A-0 297 030, EP-A-0 356 391, EP-A-0 462 053, EP-A-0 506 617 and EP-A-0 536 085. These include compounds containing unsubstituted glycidyl groups and/or methyl group-substituted glycidyl groups. The glycidyl compounds preferably have a molecular weight from 200 to 1200, more preferably from 200 to 1000, and may be solid or liquid. Their epoxy content is preferably at least three equivalents per kilogram of the compound, preferably at least four equivalents per kilogram and, more preferably, at least five equivalents per kilogram. Preferred glycidyl compounds are those which contain glycidyl ether and/or glycidyl ester groups. A glycidyl compound may in this case also contain both kinds of glycidyl groups, for example 4-glycidyoxybenzoic acid glycidyl ester. Polyglycidyl esters containing 1-4 glycidyl ester groups are preferred, in particular diglycidyl ester and/or triglycidyl ester.

The preferred diglycidyl esters are preferably derived from aromatic, araliphatic, cycloaliphatic, heterocyclic, heterocyclic-aliphatic or heterocyclic-aromatic dicarboxylic acids containing 6 to 20, preferably 6 to 12, ring carbon atoms, or from aliphatic dicarboxylic acids containing 2 to 10 carbon atoms. Compounds of this type are commonly known and are described, inter alia, in U.S. patent US-A-3,859,314 or in DE-A-31 26 411. Examples of suitable dicarboxylic acids are phthalic acid, isophthalic acid, terephthalic acid, 2,5-dimethylphthalic acid, 5-tert-butylisophthalic acid, naphthalene-2,6-dicarboxylic acid, naphthalene-1,8-dicarboxylic acid, naphthalene-2,3-dicarboxylic acid, diphenyl ether-4,4'-dicarboxylic acid, diphenyl-2,2'-dicarboxylic acid, tetrachlorophthalic acid, 2,5-dichlorophthalic acid, ortho-, meta- or para-phenylenediacetic acid, oxalic acid, malonic

acid, succinic acid, adipic acid, 2,2,4-trimethyladipic acid, 2,4,4-trimethyladipic acid, sebacic acid, azelaic acid, fumaric acid, maleic acid and compounds such as the dicarboxylic acids obtainable by adding acrylonitrile or acrylate to compounds containing hydrogen atoms which can be activated, such as ketones, nitrogen compounds, diols or dithiols; tetrahydrophthalic acid, methyltetrahydrophthalic acid, hexahydrophthalic acid, methylhexahydrophthalic acid, endomethylenehexahydrophthalic acid, hexahydroterephthalic acid, hexahydroisophthalic acid, thiophene-2,5-dicarboxylic acid, furan-2,5-dicarboxylic acid, furan-3,4-dicarboxylic acid, pyrazine-3,4-dicarboxylic acid; 1,3-bis(carboxyethyl)hydantoin, 1,1-methylenebis[3-(p-glycidyloxycarbonylbenzyl)-5,5-dimethylhydantoin], each of which is unsubstituted or alkyl-substituted in 5-position, and other dicarboxylates containing one or several hydantoin ring(s), and N,N'-bis(p-glycidyloxycarbonylbenzoyl)isophoronediamine.

Particularly preferred are terephthalic acid diglycidyl ester or isophthalic acid diglycidyl ester or 1,4-hexahydrophthalic acid diglycidyl ester or oxalic acid diglycidyl ester or adipic acid diglycidyl ester or sebacic acid diglycidyl ester or azelaic acid diglycidyl ester or succinic acid diglycidyl ester.

Preferred are also glycidyl esters containing at least three glycidyl groups per molecule, for example polyglycidyl ester containing three or four glycidyl groups, in particular trimellitic acid triglycidyl ester, trimesic acid triglycidyl ester and pyromellitic acid tetraglycidyl ester. The preparation of the cited glycidyl compounds is known per se. Preferred glycidyl compounds and their combinations are described, inter alia, in P.-G. Gottis, J.-A. Cotting, FATIPEC Congress (1996), 23<sup>rd</sup> (Vol.B), B216-B231 (ISSN:0430-222), "Solid solutions of glycidyl compounds as TGIC alternatives in polyester powder coatings".

It is particularly preferred to use combinations of tris(2-oxo-1,3-dioxolanyl-4-methyl)isocyanurate with a mixture of a diglycidyl compound and a triglycidyl compound, for example a mixture of diglycidyl terephthalate and trimellitic acid triglycidyl ester, and to use these compounds in a weight ratio of diglycidyl compound to triglycidyl ester of 4 : 1 to 1 : 10, and preferably of about 3 : 1.

In principle, the above catalysts for the reaction of the cyclic carbonates with carboxylic acids can also be used for the glycidyl compounds. Examples of preferred catalysts which accelerate the crosslinking reaction of the glycidyl compounds with the carboxyl-containing



polymers are, however, Actiron® NXJ-60 (2-propylimidazole), Actiron® NXJ-60 P (60 % by weight 2-propylimidazole on 40 % by weight of solid substrate), Accelerator® DT 3126 (a commercially available and per se known alkyl ammonium bromide masterbatch), triphenylphosphine or ethyltriphenylphosphonium bromide, in order to enable a sufficiently fast curing reaction even at relatively low temperatures, e.g. in the range from 60°C to 160°C. These catalysts are often an organic amine or a derivative of an amine, preferably a tertiary amine or an ammonium salt or a nitrogen-containing heterocyclic compound. Preferred catalysts for the reaction of epoxy groups with carboxyl groups are phenylimidazole, N-benzyl dimethylamine and 1,8-diazabicyclo[5,4,0]-7-undecene, where required on a substrate, e.g. silicate substrate. The catalyst, or a catalyst mixture, is usefully added in an amount of about 0.1 to 10 % by weight, preferably of 0.5 to 5 % by weight and, most preferably, of about 0.4 % by weight, based on the weight of the glycidyl compound.

The above-described components are used in heat-curable compositions, in particular in paint systems, preferably in powder coating compositions, which contain as binder a carboxyl-containing polymer, preferably a carboxyl-terminated polyester and/or a carboxyl-containing acryl resin, reacting with the novel crosslinking agent(s) with crosslinking.

The acryl resin is in this case an acrylate polymer or a methacrylate polymer, preferably a copolymer of one or more than one acrylate and/or methacrylate, preferably of the corresponding alkyl esters containing 1 to 18, preferably 1 to 8, carbon atoms in the alkyl group, with acrylic acid and/or methacrylic acid and, optionally, with additional ethylenically unsaturated comonomers, and has e.g. a molecular weight (average number  $M_n$  from GPC measurement with polystyrene calibration) of 500 to 30000, preferably of 1000 to 10000. Said acryl resin furthermore preferably contains 0.2 to 6 equivalents of free carboxyl groups. The glass transition temperature of the acrylate polymers and methacrylate polymers is usefully above 20°C and is preferably in the range from 30 to 100°C. Examples of suitable (meth)acrylate monomers are ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate and, in particular,  $C_1$ - $C_4$ alkylmethacrylates, such as methyl methacrylate, ethyl methacrylate or butyl methacrylate. (Meth)acrylate derivatives containing the silane groups can also be used. Suitable ethylenically unsaturated comonomers are, for example, acrylo- or methacrylonitriles and vinyl compounds. Preferred comonomers are vinyl aromatic compounds, in particular styrenes. The above-cited polymers can be prepared in known manner, for example by polymerising the monomers dissolved in suitable organic solvents,

preferably in toluene or in mixtures of 1-methoxy-2-propanol, 1-methoxy-2-propyl acetate and methyl isobutyl ketone (for example at a weight ratio of 70/20/10) in the presence of a suitable initiator, for example dicumyl peroxide, and of a chain transfer reagent, such as thioglycolic acid. They can also be polymerised in the melt.

The carboxyl group-containing polyester polymers preferably have an acid number (indicated in mg KOH/g polyester) of 10 to 100 and a molecular weight (number average  $M_n$ ) of 2000 to 10000. The ratio  $M_w$  (weight average of the molecular weight) to  $M_n$  in these polyesters is usually from 2 to 10. The polyesters are usefully solid at room temperature and preferably have a glass transition temperature from 35 to 120°C, more preferably from 40 to 80°C. They are condensates of polyols with dicarboxylic acids and, optionally, of polyfunctional carboxylic acids or the corresponding carboxylic anhydrides. Suitable polyols are, for example, ethylene glycol, diethylene glycol, the propylene glycols, butylene glycols, 1,3-butanediol, 1,4-butanediol, neopentyl glycol, isopentyl glycol, 1,6 hexanediol, glycerol, hexanetriol, trimethylolethane, trimethylolpropane, erythritol, pentaerythritol, cyclohexanediol or 1,4-dimethylcyclohexane. Suitable dicarboxylic acids are, for example, isophthalic acid, terephthalic acid, phthalic acid, methylphthalic acids, tetrahydrophthalic acid, hexahydrophthalic acid methyltetrahydrophthalic acids, e.g. 4-methyltetrahydrophthalic acid, cyclohexanedicarboxylic acids, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, dodecanedicarboxylic acid, fumaric acid, maleic acid or 4,4'-diphenyldicarboxylic acid, and the like. Suitable tricarboxylic acids are, for example, aliphatic tricarboxylic acids, such as 1,2,3-propanetricarboxylic acid, aromatic tricarboxylic acids, such as trimesic acid, trimellitic acid and hemimellitic acid, or cycloaliphatic tricarboxylic acids, such as 6-methylcyclohex-4-ene-1,2,3-tricarboxylic acid. Suitable tetracarboxylic acids are, for example, pyromellitic acid or benzophenone-3,3',4,4'-tetracarboxylic acid. Commercially available polyesters are often based on neopentyl glycol and/or trimethylolpropane as essential alcoholic components and on adipic acid and/or terephthalic acid and/or isophthalic acid and/or trimellitic acid as essential acid components.

The novel curable compositions can furthermore contain other customary additives, for example light stabilisers, colourants, pigments, e.g. titanium dioxide, degassing agents, e.g. benzoin, adhesives, thixotropic agents and/or flow control agents. The novel curable compositions may also contain a suitable inert solvent or solvent mixture, for example xylene, butyl acetate, isobutanol, 1-methoxy-2-propanol, 1-methoxy-2-propylacetate or methyl isobutyl ketone (MIBK).

The novel curable compositions may be used in the conventional technological fields of curable epoxy resin compositions, in particular for paint systems, preferably for powder coating compositions. Powder coating compositions can be prepared by simple blending of the components, e.g. in a ball mill. Another and more preferred possibility is to melt the components together and to blend them until they are homogeneous, preferably in an extruder, e.g. in a Buss Co-kneader, and then to cool the melt and comminute it. The powder coating composition mixtures preferably have an average particle size in the range from 0.015 to 500  $\mu\text{m}$ , preferably from 5 to 100  $\mu\text{m}$ .

Depending on the application, the powder coating compositions are cured on the article to be coated at a temperature of at least 100°C, preferably in the range from 150°C to 250°C.

Curing usually requires about 5 to 60 minutes. Materials suitable for coating are all materials which are stable at the temperatures required for curing, in particular metals and ceramics.

In particular where polyesters building units are used which consist to 50 % by weight, preferably to 90 % by weight and more, of neopentandiol and aromatic or cycloaliphatic dicarboxylic acids, preferably of terephthalic acid, and which are commercially available e.g. as Crylcoat<sup>®</sup> types (UCB) or under names such as Uralac<sup>®</sup> (DSM), Alftalat<sup>®</sup> (Vianova) or Grilesta<sup>®</sup> (EMS), powder coating compositions are obtained which yield weather-resistant and particularly flexible coatings which are suitable for outdoor applications, which is the case both under sudden and under prolonged mechanical stress.

The following Examples illustrate the invention.

Figure 1 shows a comparison between the carbon dioxide liberation when (i) using tris(2-oxo-1,3-dioxolanyl-4-methyl)isocyanurate and ethyltriphenylphosphonium bromide separately in accordance with formulation C, and (ii) when using the novel formulation D.

Example 1 (Preparation of a crosslinking agent (tris[2-oxo-1,3-dioxolanyl-4-methyl]isocyanurate) which comprises the catalyst (ethyltriphenylphosphonium bromide, ETPPBr) in dissolved form.)

20 Parts per weight of tris(2-oxo-1,3-dioxolanyl-4-methyl)isocyanurate (TGIC-CO<sub>2</sub>), prepared according to WO 97/24408, are dissolved, with stirring, in 200 parts per weight of  $\gamma$ -butyrolactone (Fluka 20741) at 130°C. Subsequently, 1 part per weight of ethyltriphenylphosphonium bromide (Chemconserve CV, P.O.B. 566, 2280 AN Rijswijk, Netherlands), corresponding to a catalyst concentration of 5 % by weight, are added and the

mixture is stirred at the same temperature until it is completely dissolved. The solution so obtained is concentrated to dryness in a rotary evaporator, yielding the product, i.e. a novel crosslinking agent, in the form of a fine powder.

Example 2 (Use of the product of Example 1 as crosslinking agent for powder coating compositions based on polyesters.)

a) The substances listed in Table 1 under formulation F are mixed in the cited amounts in a mixer, using, as stated in Table 1, 2.33 % by weight of the novel crosslinking agent prepared in Example 1. To homogenise the mixture, it is extruded twice at 90°C in a twin-screw extruder (Prism TSE 16 PC). The cooled extrudate is ground in an ultracentrifugal mill (Retsch ZSM 1000) to an average particle size of about 40 µm. Particles larger than 100 µm are removed by sieving. The gel time of the powder coating composition at 180°C (in accordance with ISO norm 8130) is 240 seconds. The powder coating composition is sprayed electrostatically on test panels (Q-panel, of Q-Panel). The corresponding stoving conditions and coating thicknesses and the resulting properties of the coatings are compiled in Table 2, under F. Additional properties are listed in Table 3.

b) The powder coating formulations B, D, E and G listed in Table 1 are prepared in analogy to Example 1a). The stoving conditions, coating thicknesses and properties of the coatings are also listed in Table 2, under B, D, E, and G, respectively. Additional properties are compiled in Table 3.

Example 3 (Comparison Example)

The process described in Example 2 is repeated (i) using the formulation C and (ii) using the formulation A, each according to Table 1, tris(2-oxo-1,3-dioxolanyl-4-methyl)isocyanurate and ethyltriphenylphosphonium bromide being added separately to the formulation. The corresponding stoving conditions, coating thicknesses and the resulting properties of the coatings are compiled in Table 2, under C, resp. A. Additional properties are listed in Table 3. It is found that the properties of the coatings of the formulations C and A, obtained according to this Example 3, are markedly inferior to those of the coatings of formulation F resp. B of Example 2a). Analogous comparison data are obtained for the coatings D, E and

G if tris(2-oxo-1,3-dioxolanyl-4-methyl)isocyanurate and ethyltriphenylphosphonium bromide are added separately to the formulation in the comparison test.

Table 1 (Powder coating formulations)

formulation [% by weight]	A	B	C	D	E	F	G
polyester %	CC 801 <sup>1)</sup> 61.73	CC 801 <sup>1)</sup> 61.73	CC 801 <sup>1)</sup> 60.66	CC 801 <sup>1)</sup> 86.74	CC 801 <sup>1)</sup> 60.60	CC 801 <sup>1)</sup> 60.67	CC 801 <sup>1)</sup> 86.89
PT 910 <sup>2)</sup> , %, 3 mm coating thickness	---	---	4.94	7.07	4.94	4.94	7.08
TGIC-CO <sub>2</sub> %	5.63	---	2.21	---	---	---	---
TGIC-CO <sub>2</sub> with ETPPBr, %	---	5.64 5% cat.	---	3.49 10% cat.	2.44 10% cat.	2.33 5% cat.	3.33 5% cat.
ETPPBr %	0.28	---	0.12	---	---	---	---
benzoin %	1.07	1.07	1.05	1.50	1.05	1.05	1.50
Resiflow PV 88 <sup>3)</sup> %	0.86	0.86	0.84	1.20	0.84	0.84	1.20
TiO <sub>2</sub> [Kronos 2160] <sup>4)</sup> , %	30.70	30.70	30.17	---	30.14	30.18	---

1) Crylcoat®, of UCB, Belgium;

2) Ciba Specialty Chemicals, Switzerland, mixture of diglycidyl terephthalate and trimellitic acid triglycidyl ester according to P.-G. Gottis, J.-A. Cotting, FATIPEC Congress (1996), 23<sup>rd</sup> (Vol.B), B216-B231 (ISSN:0430-222)<sup>3)</sup>;

3) flow control agent, Worlée

4) according to Kronos Information of 13.05.94 about Kronos® 2160

TGIC-CO<sub>2</sub> = tris(2-oxo-1,3-dioxolanyl-4-methyl)isocyanurate;

ETPPBr = ethyltriphenylphosphonium bromide

Table 2 (Properties of the coatings)

	A	B	C	D	E	F	G
gel time at 180°C	> 600 s	> 600 s	110 s	80 s	90 s	240 sec	140 s
cure	15 min. / 200°C	15 min. / 200°C	15 min. / 200°C	10 min. / 200°C	10 min. / 200°C	15 min. / 200°C	15 min. / 200°C
coating thickness [µm]	57	54	59	61	68	67	64
substrate	Q-panel	Q-panel	Q-panel	Q-panel	Q-panel	Q-panel	Q-panel
gloss 60°	89	98	88	98	86	96	104
Yellowness Index YI	6.7	3.4	5.2	---	2.8	3.7	---
flow [note]	6	4	12	12	12	10	10
rev. impact [kg.cm]	<5	<5	40	>160	>140	>160	>160
acetone test, 1 min. [note]	5	5	3	3	2	3	3
aspect	full of bubbles	no bubbles	O.K.	O.K.	O.K.	O.K.	O.K.

YI = Yellowing Index

Table 3 (Curing at different stoving temperatures)

formulation C:	15 min./160°C	15 min./180°C	15 min./200°C
rev. impact [kg.cm]	<5	5	40
acetone test	3	3	3

formulation D:	10 min./160°C	10 min./180°C	10 min./200°C
rev. impact [kg.cm]	>160	>160	>160
acetone test	3	3	3

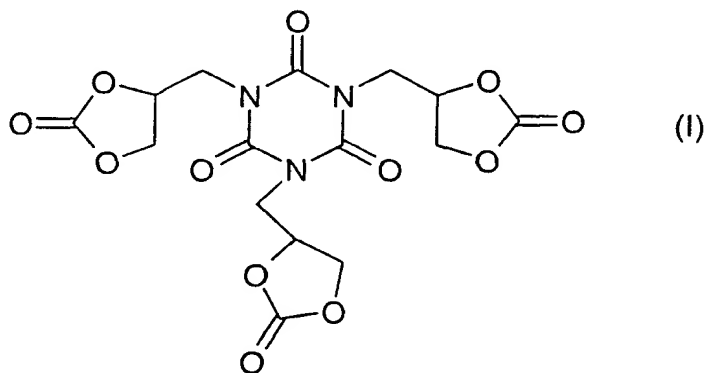
formulation E:	10 min./160°C	10 min./180°C	10 min./200°C
rev. impact [kg.cm]	<5	20	>140
acetone test	3	2	2

formulation F:	15 min./160°C	15 min./180°C	15 min./200°C
rev. impact [kg.cm]	<5	30	>160
acetone test	3	3	3

formulation G:	15 min./160°C	15 min./180°C	15 min./200°C
rev. impact [kg.cm]	15	>160	>160
acetone test	3	3	3

What is claimed is

1. A crosslinking agent for heat-curable carboxyl-containing polymers, in particular for systems containing carboxyl-terminated polyesters, carboxyl-containing acrylate polymers and/or methacrylate polymers, which crosslinking agent consists at least of one cyclocarbonate group-containing isocyanurate compound, which is characterised in that said cyclocarbonate group-containing isocyanurate compound contains at least one catalyst in dissolved or dispersed form, which has been incorporated separately into the isocyanurate compound prior to the crosslinking reaction.
2. A crosslinking agent according to claim 1, wherein the cyclocarbonate group-containing isocyanurate compound has a melting point of at least 120°C, preferably of at least 130°C and, particularly preferably, of at least 140°C.
3. A crosslinking agent according to claim 1, wherein the cyclocarbonate group-containing isocyanurate compound is a tris(2-oxo-1,3-dioxolanyl-4-methyl)isocyanurate of formula (I):



4. A crosslinking agent according to claim 1, wherein the cyclocarbonate group-containing isocyanurate compound is a compound analogous to the compound of formula (I) and contains only one single or two cyclocarbonate group(s), the remaining groups being in the form of glycidyl radicals, which analogous compound preferably contains not more than 35 mol-%, particularly preferably not more than 5 mol-% of epoxy groups.

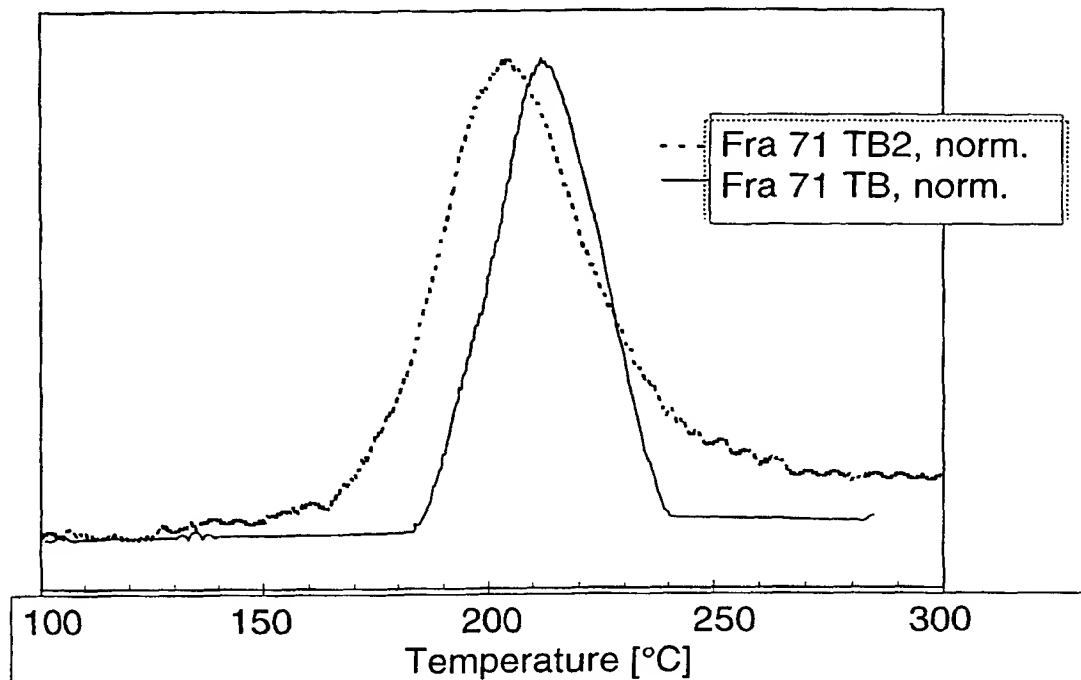
5. A crosslinking agent according to claim 1, which comprises the catalyst in an amount from 0.01 % by weight to 20 % by weight, preferably from 0.1 % by weight to 10 % by weight, more preferably from 5 % by weight, based on the weight of the cyclocarbonate group-containing isocyanurate compound.
6. A crosslinking agent according to claim 1, which comprises a catalyst which acts selectively predominantly or exclusively on the cyclocarbonate group-containing isocyanurate compound.
7. A crosslinking agent according to claim 1, wherein the catalyst which accelerates the crosslinking reaction of the cyclocarbonate group-containing isocyanurate compounds with the carboxyl-containing polymers is a compound acting as a Lewis acid or as a Lewis base,  $\text{FeSO}_4$ ,  $\text{NaHSO}_4$ ,  $\text{CeSO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{ZnCl}_2$ ,  $\text{Na}_2\text{CO}_3$ , phosphonic acid, p-toluenesulfonic acid, dimethylsulfonic acid, an ammonium salt and/or a phosphonium salt.
8. A crosslinking agent according to claim 1, wherein the catalyst which accelerates the crosslinking reaction of the cyclocarbonate group-containing isocyanurate compounds with the carboxyl-containing polymer is a tetraalkyl ammonium halide, an aryl- and alkyl-substituted ammonium halide and/or a phosphonium salt, preferably a phosphonium halide and, most preferably, an ethyltriphenylphosphonium bromide.
9. A process for the preparation of a crosslinking agent according to claim 1, which comprises dissolving a cyclocarbonate group-containing isocyanurate compound in a suitable solvent, dissolving or dispersing therein at least one catalyst and then removing the solvent again.
10. The crosslinking agent prepared or obtainable according to claim 9.
11. Use of the crosslinking agent according to any one of claims 1-8 and 10 as hardener for heat-curable carboxyl-containing polymers, in particular as hardener in systems containing carboxyl-terminated polyesters, carboxyl-containing acrylate and/or methacrylate polymers, preferably in corresponding heat-curable paint systems, in particular powder coating compositions.



- 1/1 -

Fig. 1

TG-MS Measurement (Heating rate: 10°/min., Direct Inlet)

Y-Axis = Normalized CO<sub>2</sub> Evolution (arbitrary units)

Dotted line: Formulation D (corresp. to invention),

Peak-Maximum: 203.8°C

Normal line: Formulation C,

Peak-Maximum: 221.3°C